

STUDIES ON MODIFIERS AND TACKIFIERS FOR GR-S

I. MODIFIERS. MERCAPTANS FROM OLEFIN SULFIDES

II. TACKIFIERS. THE RELATIONSHIP BETWEEN RESIN
STRUCTURE AND TACKIFIER ACTIVITY

BY

JOHN BENJAMIN ZIEGLER, JR.

B. S., University of Rochester, 1939

M. S., University of Illinois, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1946

URBANA, ILLINOIS

1946

STUDIES ON MODIFIERS AND TACKIFIERS FOR GR-S

I. MODIFIERS. MERCAPTANS FROM OLEFIN SULFIDES

II. TACKIFIERS. THE RELATIONSHIP BETWEEN RESIN
STRUCTURE AND TACKIFIER ACTIVITY

BY

JOHN BENJAMIN ZIEGLER, JR.

B. S., University of Rochester, 1939

M. S., University of Illinois, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1946

URBANA, ILLINOIS

1946

ACKNOWLEDGMENT

The author is deeply grateful to Professor H. R. Snyder, who directed this investigation, for his helpful advice and constant encouragement throughout its course.

He is indebted to Dr. M. M. Brubaker of the DuPont Experimental Station for the determination of the infrared absorption spectra and to Dr. Foil A. Miller of this Laboratory for the interpretation of these curves. He is also indebted to Dr. J. N. Street of the Firestone Tire and Rubber Company for the tackifier evaluation.

He is glad to make known his appreciation to Dr. H. A. Laitinen and Mr. Wendell Jennings who kindly performed the mercaptan titrations.

The work described in this thesis was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.



I. MODIFIERS. MERCAPTANS FROM OLEFIN SULFIDES.

INTRODUCTION

During the course of World War II it became necessary to develop commercially feasible methods for the preparation of mercaptans for use in the synthetic rubber industry as modifiers. The preparation of olefin sulfides from olefin oxides was the subject of a patent¹ issued in 1936, and it seemed likely that compounds containing active hydrogen atoms could be added to these olefin sulfides with the formation of mercaptans containing hetero atoms in the position β to the thiol group. As a matter of fact the patent literature discloses methods for the addition of amines² and mercaptans³ to olefin sulfides to form more complex mercaptans.

DISCUSSION

As a result of the present research it has been found possible to add mercaptans and alcohols to olefin sulfides with the formation in good yield of mercaptans, many of which were suitable as modifiers in the manufacture of GR-S rubber.

The previously mentioned patent procedure³ for the addition of mercaptans to olefin sulfides, which involved heating the reactants in an inert solvent at 100-200°, did not give good results in this laboratory. The two successful procedures developed in the present research involved (1) refluxing the reactants in absolute alcohol solution in the presence of a trace of sodium ethylate, and (2) heating the reactants in the presence of a trace of boron trifluoride, added as the diethyl ether or acetic acid complex. Substances resulting from the reaction between more than one molecule of olefin sulfide per molecule of mercaptan were isolated from the reaction mixtures; the formation of these higher addition products was suppressed by the use of an excess of the mercaptan. Mercaptans were added to isobutylene and cyclo-

hexene sulfides. The addition products of isobutylene sulfide were mixtures of approximately equal amounts of primary and tertiary mercaptans. The composition of the mixtures was determined by the method of Kolthoff⁴ which is based on the fact that primary mercaptans react with iodine with the formation of disulfides while tertiary mercaptans yield sulfenyl iodides.

Primary alcohols were added to isobutylene sulfide by heating a mixture of the two reactants in the presence of a small amount of the diethyl ether or acetic acid complex of boron trifluoride. The Kolthoff⁴ titration indicated that the products were almost entirely primary mercaptans.

BIBLIOGRAPHY

1. French Patent No. 797,621. Chem. Abstr. **30**, 7122.
2. German Patent No. 631,016. Chem. Abstr. **30**, 6008.
3. German Patent No. 696,774. Chem. Abstr. **35**, 5909.
4. Kolthoff and Harris, private communication.

II. TACKIFIERS. THE RELATIONSHIP BETWEEN RESIN STRUCTURE AND TACKIFIER ACTIVITY.

INTRODUCTION

The German tack resin, Koresin, is prepared by the condensation of acetylene with *p*-*tert*-butylphenol in the presence of the acid catalyst, zinc naphthenate. It is the belief of the German chemist, Reppe,¹ that the reaction takes place through the intermediate formation and subsequent resinification of 2-hydroxy-5-*tert*-butylstyrene. Marvel, Gander and Chambers² have found evidence which indicates that the presence of free phenolic hydroxyl groups is a feature of the Koresin molecule which is essential for its tackifying activity. They showed that Koresin, which is a good tackifier, possesses considerable free hydroxyl as evidenced by its

infrared absorption spectrum. On the other hand if acetylene is condensed with *p*-*tert*-butylphenol in the presence of an alkaline catalyst such as potassium hydroxide, the resulting resin has no hydroxyl band in its infrared spectrum and is a very poor tackifier.

DISCUSSION

If Reppe's view¹ of the mode of formation of Koresin is correct, the resinification of 2-methoxy-5-*tert*-butylstyrene in the presence of zinc naphthenate should yield a resin similar in structure to Koresin but containing no free phenolic hydroxyl groups. This styrene derivative was prepared by the chloroethylation reaction³ which involves the treatment of *p*-*tert*-butylanisole with acetaldehyde and hydrogen chloride in the presence of phosphoric acid, followed by dehydrohalogenation of the intermediate chloroethyl compound by heating with pyridine. The resin formed from this compound was found to be a poor tackifier and the infrared absorption spectrum contained no hydroxyl band. However, other differences between the spectrum of this compound and that of Koresin made it impossible to state with absolute certainty that the difference in tackifying potency of the two resins was due to the presence or absence of free phenolic hydroxyl groups. Nevertheless, this observation constitutes further evidence of the probable importance of such groups. An attempt to demethylate this resin by treatment with hydrogen bromide in chloroform-glacial acetic acid solution resulted in the liberation of only a very small amount of free hydroxyl.

Resinification of 2-hydroxy-5-*tert*-butylphenylmethylcarbinol and 2-hydroxy-5-*tert*-butylstyrene should furnish resins of interest in connection with the question of the relation of phenolic hydroxyl groups to tack-production. It should be possible to prepare these substances from 2-hydroxy-5-*tert*-butylacetophenone. This ketone was prepared by the acetylation of *p*-*tert*-butylphenol with glacial acetic acid in the presence of boron trifluoride according to the general procedure of von Auwers,⁴ and also by the Fries rearrange-

ment of *p-tert*-butylphenylacetate using boron trifluoride as the catalyst. In the procedure first named, extensive rearrangement occurred; in addition to the desired product a number of other substances were isolated. They were (1) *o*-hydroxyacetophenone, (2) an isomeric monobutyl monoacetylphenol, and (3) a dibutyl monoacetylphenol. The structures of these last two compounds are unknown.

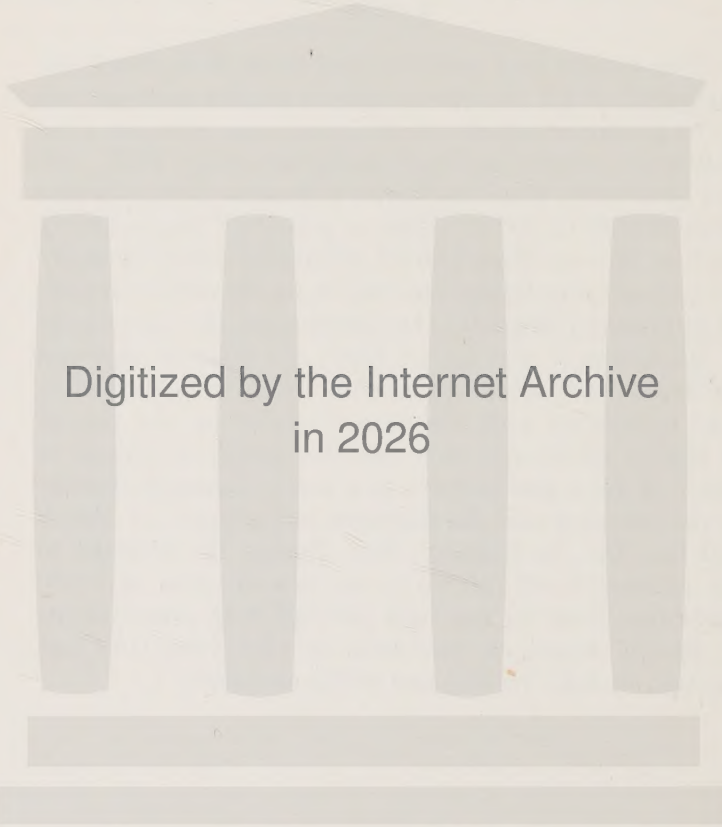
This is an abstract of the unrestricted portion of the thesis.

BIBLIOGRAPHY

1. Reppe, "Advances in Acetylene Chemistry," ORR Report No. G-1, July 25, 1945, p. 10.
2. Marvel, Gander and Chambers, private communication.
3. Quelet and Ducasse, Compt. rend. **208**, 1317 (1939).
4. von Auwers, Pötz and Noll, Ann. **535**, 228 (1938).

VITA

The author was born in Rochester, New York, on January 2, 1917. His elementary education was received in the grammar schools of Rochester and of Santa Ana, California, where he lived during the year 1927. He was graduated from Rochester's Monroe Junior-Senior High School in 1933. After a period of postgraduate work at Monroe High and an additional period of study in the Rochester Collegiate Center, an extension division of Syracuse University, he enrolled in the University of Rochester in the fall of 1935. In 1939 he received the degree of Bachelor of Science with Distinction from that institution and this was followed by the degree of Master of Science from the University of Illinois in 1940. After a period spent as a junior research chemist in the research and development laboratories of Merck and Co., Inc., in Rahway, New Jersey, he returned to the University of Illinois in the late summer of 1943. Since that time he has held the full time appointment of Special Research Assistant in Chemistry and has worked on both NDRC and WPB contracts.



Digitized by the Internet Archive
in 2026

